

US 19001/TC5431

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent application of: **Mario Sacchetti et al.**)
Serial Number: **Not yet assigned**)
Filed: **January 8, 2002**)
US National Phase of International Patent)
Application No: **PCT/EP01/05254**)
Filed: May 7, 2001)
For: **PRE-POLYMERIZED CATALYST**)
COMPONENTS FOR THE)
POLYMERIZATION OF OLEFINS)

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January 8, 2002

PRELIMINARY AMENDMENT

This is a preliminary amendment to US 19001, filed herewith, which is the US National Phase of the International Patent Application No. PCT/EP01/05254, filed on May 7, 2001, and claiming priority to European Application EP 00201702.8 filed on May 12, 2000.

In the Specification

Please amend the specification as follows:

Please replace the paragraph beginning at page 1, line 17 and ending at page 2, line 8 with the following paragraph.

--In the attempt to solve these problems, the catalyst is pre-polymerized under controlled

conditions, so as to obtain pre-polymerized catalysts purposed to have good morphology. In fact, it is believed that after the pre-polymerization, the catalysts increase their resistance in such a way that the tendency to break under polymerization conditions is decreased. As a consequence, also the formation of fine particles would be reduced. In addition, it is hoped that also the bulk density of the final polymers is improved. In principle the catalyst component could be pre-polymerized with any olefin, however, in practice, the non-stereospecific catalysts are always pre-polymerized with ethylene. In fact, in the art it is believed that if prochiral olefins like propylene would be pre-polymerized with non-stereospecific catalyst, the amorphous polymer produced would negatively affect the performance of the catalysts both in terms of activity and morphological properties. The pre-polymerization with ethylene of a non-stereospecific catalyst however does not fully solve the problems mentioned before. In USP 4,325,837 for example, as it is apparent from table 14A and 14B, the use of a non-stereospecific catalyst pre-polymerized with ethylene to an extent of lower than 50% b.w., based on the weight of the total pre-polymerized catalyst, is not always satisfactory because the yields and the morphological properties of the polymer produced with the pre-polymerized catalyst are in certain cases lower than that of the non-pre-polymerized one. In the same patent it is said (column 37 lines 57-60) that the use of a pre-polymerized catalyst is of no advantage with respect to the non pre-polymerized one. In addition to these problems, it must be noted that in view of the very high reactivity of ethylene the pre-polymerization with this monomer can give some difficulties in keeping the mild conditions that are generally used in the pre-polymerization in order to reach the desired properties of the catalyst.--

Please replace the paragraph beginning at page 2, line 14 and ending at line 19 with the following paragraph:

--It is therefore an object of the present invention a pre-polymerized catalyst component for the polymerization of ethylene, optionally in mixtures with olefins $\text{CH}_2=\text{CHR}$, wherein R is a C1-C12 alkyl group, characterized by comprising a non-stereospecific solid catalyst component, comprising Ti, Mg and a halogen, which is pre-polymerized with an alpha olefin $\text{CH}_2=\text{CHR}^1$ wherein R^1 is a C1-C8 alkyl group, to such an extent that the amount of the α -olefin pre-polymer is up to 100g per g of said solid catalyst component.--

In the Claims

Please amend claims 1-18 to read as follows:

- 1. (Amended) A pre-polymerized catalyst component for the polymerization of ethylene optionally in mixtures with olefins $\text{CH}_2=\text{CHR}$, wherein R is a C1-C12 alkyl group, comprising a non-stereospecific solid catalyst component, comprising Ti, Mg and a halogen, which is pre-polymerized with an α -olefin $\text{CH}_2=\text{CHR}^1$ wherein R^1 is a C1-C8 alkyl group, and the amount of the α -olefin pre-polymer is up to 100g per g of said solid catalyst component.
2. (Amended) The pre-polymerized catalyst component according to claim 1 in which the amount of the α -olefin polymer is less than 15 g per g of said solid catalyst component.

3. (Amended) The pre-polymerized catalyst component according to claim 2 in which the amount of the α -olefin polymer is from 0.8 to 4 g per g of solid catalyst component.
4. (Amended) The prepolymerized catalyst component according to claim 1 comprising a titanium compound and a magnesium dihalide.
5. (Amended) The pre-polymerized catalyst component according to claim 1 in which the magnesium dihalide is magnesium dichloride in active form and the titanium compound is selected from the compounds of formula $\text{Ti}(\text{OR})_{n-y}\text{X}_y$, where R is a C1-C20 hydrocarbon group, X is a halogen, n is the valence of titanium and y is a number between 1 and n.
6. (Amended) The pre-polymerized catalyst component according to claim 5 in which the titanium compound is chosen from TiCl_4 , TiCl_3 and Ti-tetraalcoholates or Ti-chloroalcoholates of formula $\text{Ti}(\text{OR}^{\text{II}})_a\text{Cl}_{n-a}$ where n is the valence of titanium, a is a number comprised between 1 and n, and R^{II} is a C1-C8 alkyl or aryl group.
7. (Amended) The pre-polymerized catalyst component according to claim 1 in which the solid catalyst component to be pre-polymerized has a surface area, by B.E.T. method, between 20 and 500 m^2/g , and a total porosity, by B.E.T. method, higher than 0.2 cm^3/g .
8. (Amended) The pre-polymerized catalyst component according to claim 1 in which the solid catalyst component to be pre-polymerized has a porosity (Hg method) due to pores with radius up to 10000 Å, of from 0.3 to 1.5 cm^3/g .

9. (Amended) The pre-polymerized catalyst component according to claim 1 in which the solid catalyst component is pre-polymerized with an α -olefin selected from propylene, butene-1, hexene, 4-methyl-1-pentene, and octene-1.
10. (Amended) The pre-polymerized catalyst component according claim 9 in which the α -olefin is propylene.
11. (Amended) The pre-polymerized catalyst component according to claim 1 in which the solid catalyst component to be pre-polymerized is obtained by:
- (a) reacting a compound $\text{MgCl}_2 \cdot m\text{ROH}$, wherein $0.3 \leq m \leq 1.7$ and R is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms, with a titanium compound of the formula $\text{Ti}(\text{OR}^{\text{II}})_b\text{X}_{y-b}$, in which b is comprised between 0 and 0.5, y is the valence of titanium, X is a halogen and R^{II} is a C1-C20 hydrocarbon group;
 - (b) reacting the product obtained from (a) with an Al-alkyl compound; and
 - (c) reacting the product obtained from (b) with a titanium compound of the formula $\text{Ti}(\text{OR}^{\text{II}})_n\text{X}_{y-n}$, in which R^{II} is a C1-C20 hydrocarbon group, X is a halogen, n is the valence of titanium, and y is a number between 1 and n.
12. (Amended) The pre-polymerized catalyst component according to claim 1 in which the solid catalyst component to be pre-polymerized is obtained by:
- (a) thermally dealcoholating adducts $\text{MgCl}_2 \cdot p\text{EtOH}$, where p is a number between 2 to 3.5, until forming adducts in which the alcohol content is reduced to values lower than 2 mols per mol of magnesium dihalide;
 - (b) treating the thermally dealcoholated adduct of step (a) with chemical reagents capable of reacting with the OH groups of the alcohol to dealcoholate the

adduct until the alcohol content is reduced to values which are lower than 0.5 mols; and

- (c) reacting the chemically dealcoholated adduct of step (b) with a Ti compound of formula $\text{Ti}(\text{OR}^{\text{II}})_{n-y}\text{X}_y$, where R^{II} is a C1-C20 hydrocarbon group, X is a halogen, n is the valence of titanium and y is a number between 1 and n.

13. (Amended) The pre-polymerized catalyst component according to claim 1 in which said pre-polymerization is carried out using amounts of an alkyl-Al compound such as to have an Al/Ti molar ratio from 0.001 to 50.
14. (Amended) The pre-polymerized catalyst component according to claim 13 in which the Al-alkyl compound is a trialkyl aluminum compound.
15. (Amended) The pre-polymerized catalyst component according to claim 14 in which the trialkyl aluminum compound is chosen from triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, and tri-n-octylaluminum.
16. (Amended) A process for the (co)polymerization of ethylene characterized in that it is carried out in the presence of a catalyst comprising (A) a pre-polymerized catalyst component comprising a non-stereospecific solid catalyst component, comprising Ti, Mg and a halogen, which is pre-polymerized with an α -olefin $\text{CH}_2=\text{CHR}^{\text{I}}$ wherein R^{I} is a C1-C8 alkyl group, and the amount of the α -olefin pre-polymer is no greater than 100g per g of said solid catalyst component; and (B) an Al-alkyl compound.
17. (Amended) The process according to claim 16 in which ethylene is copolymerized with olefins $\text{CH}_2=\text{CHR}$, wherein R is a C1-C12 alkyl group.

18. (Amended) The process according to claim 17 in which the olefin is chosen from propylene, butene-1, hexene-1 octene-1 and 4-methyl-1-pentene.--

Please add the following new claims 19 and 20:

- 19. (New) The pre-polymerized catalyst component according to claim 12, wherein in step (a) the alcohol content is reduced to values of from 1.5 to 0.3 mols per mol of magnesium dihalide.
20. (New) The pre-polymerized catalyst component according to claim 13, wherein the Al/Ti molar ratio is from 0.01 to 10.--

REMARKS

This preliminary amendment is being filed concurrently with Applicants' application US 19001, for which a serial number has not yet been assigned.

Typographical errors in the specification have been corrected, and claims 1-18 have been amended to better point out and more distinctly claim the present invention. New claims 19 and 20 have been added, support for which can be found in claims 12 and 13 as originally filed, and in the specification at page 5, lines 26-30 and page 7, lines 4-6. No new matter has been added by these amendments and they do not affect the scope of the claims as originally filed.

Separate pages with a marked-up version of the amended specification and claims entitled: "Version with Markings to Show Changes Made" are attached.

An early and favorable action on the merits is requested. The Applicants invite the Examiner to direct any questions or comments to the undersigned at the telephone number given below.

It is not believed that any fee is required for entry and consideration of this Amendment; nevertheless, the Commissioner is hereby authorized to charge U.S. PTO Deposit Account 08-2336 in the amount of any such required fee.

Respectfully submitted,

MARIO SACCHETTI et al.

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I hereby certify that this correspondence is being deposited with the United States Postal Service as "**Express Mail Post Office to Addressee**" in an envelope addressed to: U.S. Patent and Trademark Office, Box PCT, Commissioner for Patents, P.O. Box 2327, Arlington, VA 22202 on January 8, 2002 with the number of the Express Mail label being **EK 794120383US**.

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**VERSION WITH MARKINGS TO SHOW CHANGES MADE
Filed on January 8, 2002**

In the Specification

Paragraph beginning at page 1, line 17 and ending at page 2, line 8.

In the attempt to solve these problems, the catalyst is pre-polymerized under controlled conditions, so as to obtain pre-polymerized catalysts purposed to have good morphology. In fact, it is believed that after the pre-polymerization, the catalysts increase their resistance in such a way that the tendency to break under polymerization conditions is decreased. As a consequence, also the formation of fine particles would be reduced. In addition, it is hoped that also the bulk density of the final polymers is improved. In principle the catalyst component could be pre-polymerized with any olefin, however, in practice, the non-stereospecific catalysts are always pre-polymerized with ethylene. In fact, in the art it is believed that if prochiral [α -olefins]olefins like propylene would be pre-polymerized with non-stereospecific catalyst, the amorphous polymer produced would negatively affect the performance of the catalysts both in terms of activity and morphological properties. The pre-polymerization with ethylene of a non-stereospecific catalyst however does not fully solve the problems mentioned before. In USP 4,325,837 for example, as it is apparent from table 14A and 14B, the use of a non-stereospecific catalyst pre-polymerized with ethylene to an extent of lower than 50% b.w., based on the weight of the total pre-polymerized catalyst, is not always satisfactory because the yields and the morphological properties of the polymer produced with the pre-polymerized catalyst are in certain cases lower than that of the non-pre-polymerized one. In the same patent it is said (column 37 lines 57-60) that the use of a pre-polymerized catalyst is of no

advantage with respect to the non pre-polymerized one. In addition to these problems, it must be noted that in view of the very high reactivity of ethylene the pre-polymerization with this monomer can give some difficulties in keeping the mild conditions that are generally used in the pre-polymerization in order to reach the desired properties of the catalyst.

Paragraph beginning at page 2, line 14 and ending at line 19.

It is therefore an object of the present invention a pre-polymerized catalyst component for the polymerization of ethylene, optionally in mixtures with olefins $\text{CH}_2=\text{CHR}$, wherein R is a C1-C12 alkyl group, characterized by comprising a non-stereospecific solid catalyst component, comprising Ti, Mg and a halogen, which is pre-polymerized with an alpha olefin $\text{CH}_2=\text{CHR}^1$ wherein $[\text{R}]\underline{\text{R}}^1$ is a C1-C8 alkyl group, to such an extent that the amount of the α -olefin pre-polymer is up to 100g per g of said solid catalyst component.

In the Claims

Claims 1-18 have been changed by deleting the characters in brackets and adding the underlined material, as reported below. Claims 19 and 20 are new. For the Examiner's convenience, even the unchanged claims have been reported in the following.

1. (Amended) A pre-polymerized catalyst component for the polymerization of ethylene optionally in mixtures with olefins $\text{CH}_2=\text{CHR}$, wherein R is a C1-C12 alkyl group, [characterized by]comprising a non-stereospecific solid catalyst component, comprising Ti, Mg and a halogen, which is pre-polymerized with an α -

olefin $\text{CH}_2=\text{CHR}^I$ wherein $[\text{R}]\underline{\text{R}}^I$ is a C1-C8 alkyl group, [to such an extent that]and the amount of the α -olefin pre-polymer is up to 100g per g of said solid catalyst component.

2. (Amended) [A]The pre-polymerized catalyst component according to claim 1 in which the amount of the α -olefin polymer is less than 15 g per g of said solid catalyst component.
3. (Amended) [A]The pre-polymerized catalyst component according to claim 2 in which the amount of the α -olefin polymer is from 0.8 to 4 g per g of solid catalyst component.
4. (Amended) [A]The prepolymerized catalyst component according to claim 1 comprising a titanium compound and a magnesium dihalide.
5. (Amended) [A]The pre-polymerized catalyst component according to claim 1 in which the magnesium dihalide is magnesium dichloride in active form and the titanium compound is selected from the compounds of formula $\text{Ti}(\text{OR})_{n-y}\text{X}_y$, where R is a C1-C20 hydrocarbon group, X is a halogen, n is the valence of titanium and y is a number between 1 and n.
6. (Amended) [A]The pre-polymerized catalyst component according to claim 5 in which the titanium compound is [selected]chosen from [the group consisting of] TiCl_4 , TiCl_3 and Ti-tetraalcoholates or Ti-chloroalcoholates of formula $\text{Ti}(\text{OR}^{\text{II}})_a\text{Cl}_{n-a}$ where n is the valence of titanium, a is a number comprised between 1 and n, and R^{II} is a C1-C8 alkyl or aryl group.
7. (Amended) [A]The pre-polymerized catalyst component according to claim 1 in which the solid catalyst component to be pre-polymerized has a surface area, by

B.E.T. method, between 20 and 500 m²/g, and a total porosity, by B.E.T. method, higher than 0.2 cm³/g.

8. (Amended) [A]The pre-polymerized catalyst component according to claim 1[or 6] in which the solid catalyst component to be pre-polymerized has a porosity (Hg method) due to pores with radius up to 10000 Å, of from 0.3 to 1.5 cm³/g.
9. (Amended) [A]The pre-polymerized catalyst component according to [any of the preceding claims]claim 1 in which the solid catalyst component is pre-polymerized with an α -olefin selected from propylene, butene-1, hexene, 4-methyl-1-pentene, and octene-1.
10. (Amended) [A]The pre-polymerized catalyst component according claim 9 in which the α -olefin is propylene.
11. (Amended) [A]The pre-polymerized catalyst component according to [any of the preceding claims]claim 1 in which the solid catalyst component to be pre-polymerized is obtained by:
 - (a) reacting a compound MgCl₂.mROH, wherein $0.3 \leq m \leq 1.7$ and R is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms, with a titanium compound of the formula Ti(OR^{II})_bX_{y-b}, in which b is comprised between 0 and 0.5, y is the valence of titanium, X is a halogen and R^{II} [has the meaning given above]is a C1-C20 hydrocarbon group;
 - (b) reacting the product obtained from (a) with an Al-alkyl compound; and[,]
 - (c) reacting the product obtained from (b) with a titanium compound of the formula Ti(OR^{II})_nX_{y-n}, in which [n, y, X and R^{II} have the meanings explained

above] R^{II} is a C1-C20 hydrocarbon group, X is a halogen, n is the valence of titanium, and y is a number between 1 and n.

12. (Amended) [A]The pre-polymerized catalyst component according to [any of the claims 1-10]claim 1 in which the solid catalyst component to be pre-polymerized is obtained by:
- (a) [the thermal dealcoholation of the]thermally dealcoholating adducts $MgCl_2 \cdot pEtOH$, where p is a number between 2 to 3.5, until forming adducts in which the alcohol content is reduced to values lower than 2 [and preferably comprised between 1.5 and 0.3]mols per mol of magnesium dihalide[,];
 - (b) [the treatment of said]treating the thermally dealcoholated adduct of step (a) with chemical reagents capable of reacting with the OH groups of the alcohol [and of further dealcoholating]to dealcoholate the adduct until the alcohol content is reduced to values which are [generally]lower than 0.5 mols; and
 - (c) [the reaction of said]reacting the chemically dealcoholated adduct of step (b) with a Ti compound of formula $Ti(OR^{II})_{n-y}X_y$, where [X, R^{II} , n, and y have the same meanings described above] R^{II} is a C1-C20 hydrocarbon group, X is a halogen, n is the valence of titanium and y is a number between 1 and n.
13. (Amended) [A]The pre-polymerized catalyst component according to [any of the preceding claims]claim 1 in which said pre-polymerization is carried out using amounts of an alkyl-Al compound such as to have an Al/Ti molar ratio from 0.001 to 50[, preferably from 0.01 to 10].
14. (Amended) [A]The pre-polymerized catalyst component according to claim 13 in which the Al-alkyl compound is a trialkyl aluminum compound.

15. (Amended) [A]The pre-polymerized catalyst component according to claim 14 in which the trialkyl aluminum compound is [selected]chosen from triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, and tri-n-octylaluminum.
16. (Amended) A process for the (co)polymerization of ethylene characterized in that it is carried out in the presence of a catalyst comprising (A) a pre-polymerized catalyst component [according to any of the preceding claims]comprising a non-stereospecific solid catalyst component, comprising Ti, Mg and a halogen, which is pre-polymerized with an α -olefin $\text{CH}_2=\text{CHR}^1$ wherein R^1 is a C1-C8 alkyl group, and the amount of the α -olefin pre-polymer is no greater than 100g per g of said solid catalyst component; and (B) an Al-alkyl compound.
17. (Amended) [A]The process according to claim 16 in which ethylene is copolymerized with olefins $\text{CH}_2=\text{CHR}$, wherein R is a C1-C12 alkyl group.
18. (Amended) [A]The process according to claim 17 in which the olefin is [selected]chosen from [the group consisting of]propylene, butene-1, hexene-1 octene-1 and 4-methyl-1-pentene.
19. (New) The pre-polymerized catalyst component according to claim 12, wherein in step (a) the alcohol content is reduced to values of from 1.5 to 0.3 mols per mol of magnesium dihalide.
20. (New) The pre-polymerized catalyst component according to claim 13, wherein the Al/Ti molar ratio is from 0.01 to 10.